

Experimental Study of Thermodiffusion and Thermoelectricity in Charged Colloids

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Abstract

The Seebeck and Soret coefficients of ionically stabilized suspension of maghemite nanoparticles in dimethyl sulfoxide are experimentally studied as a function of nanoparticle volume

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fraction. In the presence of a temperature gradient, the charged colloidal nanoparticles experience both thermal drift due to their interactions with the solvent molecules and electric forces proportional to the internal thermoelectric field. The resulting thermodiffusion of nanoparticles is observed through Forced Rayleigh scattering, while the thermoelectric field is accessed through voltage measurements in a thermocell. Both techniques provide independent estimates of nanoparticle's entropy of transfer as high as 75 meV.K^{-1} . Such a property may be used to improve the thermoelectric coefficients in liquid thermocells.

1. INTRODUCTION

The thermoelectric effect (Seebeck effect) is known to influence the thermodiffusion behavior of charged colloidal suspensions with contributions coming from both electrolytes and charged colloidal particles themselves.^{1–3} Under a thermal gradient ∇T , the thermal drift of ionic species, i , induces concentration gradients $\nabla n_i/n_i = -\alpha_i \nabla T$ (Soret effect) and an internal electric field $\mathbf{E} = \mathcal{S}_e \nabla T$ (Seebeck effect). Both Soret (α_i) and Seebeck (\mathcal{S}_e) coefficients depend on the *Eastman entropies of transfer* \widehat{S}_i ,^{2–6} which characterize the interaction of species i with the solvent.⁷ The absolute value of \widehat{S}_i generally increases with the ion size. Large Soret effects have indeed been reported experimentally in various colloidal suspensions such as silica particles, DNA molecules, polystyrene spheres and magnetic nanoparticles (ferrofluids)^{8–13} reflecting the large Eastman entropy of transfer associated with their equally large physical size (in the nm– μm range). The corresponding Seebeck coefficient, on the other hand, has rarely been studied.¹⁴

Here, we investigate one such charged colloidal suspension, namely, ionically stabilized ferrofluids in dimethyl sulfoxide (DMSO). Ferrofluids were chosen not only because of the high Soret coefficients^{13,15} of nanoparticles (NPs) but also because of their magnetic nature which may offer an additional control parameter (magnetic field¹⁶) on the thermodiffusive and thermoelectric behaviour. We determine independently the Eastman entropy of transfer of NPs \widehat{S} through (i) the Soret effect using forced Rayleigh scattering measurements and (ii) the Seebeck effect using a thermocell (see experimental section below). The values of \widehat{S} deduced from the two experiments

agree quantitatively and are almost three orders of magnitude higher than that of typical ions in electrolytes.⁴ Furthermore, we show that the thermodiffusion of NPs has a sizable influence on the Seebeck coefficient, an effect that may be used in liquid thermoelectric applications.¹⁷

2. EXPERIMENTAL SECTION

2.1. Samples

We have used ferrofluids based on well-known maghemite $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (average diameter $d = 6.7$ nm and log-normal size distribution 0.38, determined from room-temperature magnetization measurements) dispersed in DMSO. Nanoparticles are chemically synthesized first in water (see¹⁸ for methods). This dispersion gives a ferrofluid of positively charged NPs with nitrate counterions, which are then replaced by perchlorate ones following the method described in.¹⁹ At the end of the process, DMSO is added instead of water to obtain electrostatically stabilized dispersion with positively charged NP surface. The concentration of free perchloric acid in the solution was kept constant at ≈ 12.5 mM. This value was determined from the conductivity measurement in the supernatant of DMSO ferrofluid obtained after ultracentrifugation (60000 rpm, 1h30) which separates the NPs from the solvent.

2.2. Thermodiffusion measurements

The Forced Rayleigh scattering technique used to extract the Soret and the NPs diffusion coefficients is well described in Ref.²⁰ The heating light (Hg arc lamp, 100Hz modulation) creates the optical image of a grid in the sample. Owing to the optical absorption by the NPs, a temperature grating is induced in the sample. Then a NP concentration grating settles due to the Soret effect in a few seconds at the spatial scale of $\approx 50 \mu\text{m}$. Both gratings are detected by the diffraction of a weakly absorbing test laser beam. As the gratings of the temperature and the NPs concentration evolve on timescales differing by orders of magnitude, this technique enables the use of a “two-

timescale” model.²⁰ The Soret coefficient is deduced from the temporal modulation of scattered intensity at a constant spatial modulation of NPs concentration. The diffusion coefficient is determined by the relaxation time measurement of the concentration grating after the heating source is switched off.

2.3. Thermoelectric measurements

The Seebeck coefficient measurements were performed in a homemade thermocell consisting of a vertical, cylindrical Teflon cell (14 mm high and 6 mm diameter) with two ends sealed by sapphire windows, similar to the setup described in Refs.^{21,22} The ferrocene/ferrocenium (F_C/F_C^+) redox couple (2/4 mM respectively) was added to the sample in order to permit the exchange of electrons between the electrodes and the ferrofluid. These chemicals were purchased from *SigmaAldrich*; ferrocene (F_C , 98%) and ferrocenium-tetrafluoroborate (F_CBF_4 , technical grade) and used as received. The sample preparation is performed in a glovebox under a nitrogen atmosphere. It should be noted that the co-existence of the redox couple and nanoparticles did not change the redox potential (*cf.* Supporting Information I) or cause aggregation of NPs. The experiments are carried out between 30 °C and 50 °C (mean temperature) with the temperature difference between the two electrodes $\Delta T_{elect} \approx 4.3$ °C (10 °C difference between the cell extremities). The open circuit voltage is: $\Delta V = -\Lambda \Delta T_{elect}$, where Λ shall be referred to as the “*thermoelectric coefficient*”, to be distinguished from the Seebeck coefficient \mathcal{S}_e . The thermoelectric voltage was monitored over 2 hours between each temperature change. The diffusion coefficient D (see inset in Figure 1), gives the nanoparticle diffusion time $\tau = l^2/(4\pi D)$ of the order of two days for our thermocell. Thus the observed electromotive force and thermoelectric coefficient Λ correspond to those of the *initial state*.⁴

3. RESULTS AND DISCUSSION

3.1. Theoretical considerations

To analyse our experimental results, here we consider a colloidal solution containing a concentration n of charged particles with a structural diameter d and a structural charge Z_{str} (here, particles are positively charged). They are stabilized in a monovalent electrolyte solution A^+B^- . Some anions B^- are condensed within the first solvation layers of the particles, partly canceling Z_{str} thus leading to an effective charge $Z \ll Z_{str}$.²³ The remaining anions—whose Coulomb binding energy is smaller than $k_B T$ —are free. The concentrations of free anions and cations are n_- and n_+ , respectively. The electroneutrality writes:

$$Zn + n_+ - n_- = 0. \quad (1)$$

Under a temperature gradient, the particle current \mathbf{J}_i corresponding to the charged species i is:^{1,2}

$$\mathbf{J}_i = -D_i \left[\nabla n_i + n_i \frac{\hat{S}_i}{k_B T} \nabla T - n_i \frac{\xi_i e}{k_B T} \mathbf{E} \right], \quad (2)$$

where n_i is the particle density. The first term corresponds to Fick's diffusion with coefficient D_i , the second term, proportional to the “Eastman entropy of transfer” \hat{S}_i ,²⁴ represents the thermal drift, and the last term is the electric drift in the presence of a local field \mathbf{E} . The dimensionless number $\xi_i = k_B T \mu_i^{el} / e D_i$ is proportional to the ratio of the electrophoretic mobility μ_i^{el} to the diffusion coefficient D_i .² For small point-like ions the Einstein relation is valid and ξ_i is simply the ionic charge number z_i . The particle currents corresponding to small non-interacting monovalent ions are:

$$\mathbf{J}_\pm = -D_\pm \left[\nabla n_\pm + n_\pm \frac{\hat{S}_\pm}{k_B T} \nabla T \mp n_\pm \frac{e}{k_B T} \mathbf{E} \right]. \quad (3)$$

For colloidal particles ξ is of the same order of magnitude as—but not equal to—the effective charge Z .² At large volume fractions, the interaction between NPs needs to be considered. This can be

described in terms of isothermal osmotic compressibility⁵ $\chi(\phi)$, $\phi = V_{np}n$ where $V_{np} = \pi d^3/6$ is the nanoparticle volume (*cf.* Supporting information II). The ϕ dependence of the parameters \widehat{S} and ξ in eq ?? appears as:

$$\widehat{S} = \widehat{S}_0 \chi(\phi) \quad \text{and} \quad \xi = \xi_0 \chi(\phi). \quad (4)$$

Choosing a hard sphere model with Carnahan-Starling equation of state,²⁵ $\chi(\phi)$ becomes:

$$\chi(\phi_{eff}) = \frac{(1 - \phi_{eff})^4}{1 + 4\phi_{eff} + 4\phi_{eff}^2 - 4\phi_{eff}^3 + 4\phi_{eff}^4}, \quad (5)$$

where $\phi_{eff} = \phi(d_{HS}/d)^3$ represents an effective volume fraction corresponding to hard-sphere diameter $d_{HS} = d + 2\lambda_D$, where λ_D is the Debye length.

When the stationary state (st) is reached, each of the three currents expressed in eqs ?? and ?? vanishes. Combining these equations with the electroneutrality condition, eq ??, we obtain:^{1,2}

$$\mathbf{E}^{st} = \frac{1}{e} \left[\frac{Zn\widehat{S} + n_+\widehat{S}_+ - n_-\widehat{S}_-}{n_+ + n_- + \xi Zn} \right] \nabla T = \mathcal{S}_e^{st} \nabla T. \quad (6)$$

Substituting this expression in the nanoparticle current (eq ??), we obtain:

$$\frac{\nabla n}{n} = -\frac{1}{k_B T} (\widehat{S} - \xi e \mathcal{S}_e^{st}) \nabla T = -\alpha \nabla T, \quad (7)$$

where

$$\alpha = (\widehat{S} - \xi e \mathcal{S}_e^{st}) / k_B T \quad (8)$$

is the Soret coefficient. For uncharged particles only the first term is present. In a series of recent papers, Würger and coauthors^{1,2,26,27} have emphasized the importance of the second term in charged colloidal suspensions. Recent experiments by Eslahian *et al.*²⁸ on the salinity (electrolytes) effects on the thermodiffusion of polystyrene sulfonate beads appear to confirm these theoretical claims.

3.2. Thermodiffusion and thermoelectric analysis

The Soret coefficient α , determined at different NP volume fractions ϕ are reported in Figure 1 with an inset showing linear variation of the diffusion coefficient: $D(\phi) \approx 7.03 \times 10^{-12}(1 + 66.02\phi) \text{ m}^2.\text{s}^{-1}$. The variation in α was analyzed using eqs ?? and ??, with the approximation (to be justified later): $\widehat{S} >> \xi_0 \widehat{S}_+, \xi_0 \widehat{S}_- \text{ i.e.:}$

$$\alpha \approx \frac{1}{k_B T} \left[\frac{\widehat{S}(\phi_{eff})(1 + Z\tilde{n}/2)}{1 + (\xi(\phi_{eff}) + 1)Z\tilde{n}/2} \right]. \quad (9)$$

Here, we define $\tilde{n} = n/n^+$, where n^+ (H^+ ions) is kept constant. The nanoparticle structural diameter is $d = 6.7 \text{ nm}$, the Debye length is $\lambda_D = 2.1 \text{ nm}$ in a solution of 12.5 mM HClO_4 in DMSO, with dielectric constant $\epsilon = 48$, at room temperature. $\xi_0 \approx 25$ was estimated from the measurement of the electrophoretic mobility of a NP suspension at $\phi = 0.05\%$ using the laser Doppler velocimetry technique (NanoZS Malvern GB). The remaining unknown parameters Z and \widehat{S}_0 are determined through the fit (solid line in Figure 1) of the experimental data by eq ???. We obtain: $Z \approx 30$ and $\widehat{S}_0 \approx 68 \text{ meV.K}^{-1}$, or equivalently $\widehat{S}_0/\xi_0 \approx 2.7 \text{ meV.K}^{-1}$, one order of magnitude higher than typical values corresponding to electrolytes,⁴ which justifies our previous approximation: $\widehat{S} >> \xi_0 \widehat{S}_+, \xi_0 \widehat{S}_-$.

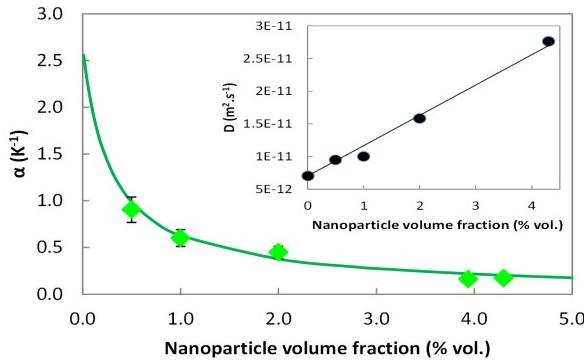


Figure 1: Soret coefficient α , and diffusion coefficient D (inset) as a function of NP volume fraction. Note that the measurements at higher concentrations ($\approx 4\%$) were performed on another set of DMSO based ferrofluids in similar ionic conditions.

In thermoelectric measurements, a temperature gradient ∇T is established across a previously isothermal, homogenous electrolyte. While the bulk distribution of different species is still uniform, an internal electric field, \mathbf{E}^{init} settles immediately within the fluid, resulting from charge accumulations at the cell boundaries.⁴ This is due to the response of ions to thermal forces $\mathbf{f}_i = \widehat{\mathcal{S}}_i \nabla T$. In open circuit conditions the total electric current: $\mathbf{J}_{elec} = Ze\mathbf{J} + e\mathbf{J}_+ - e\mathbf{J}_-$ is zero. Substituting eq ?? and eq ?? for the particle currents and taking into account the initial condition $\nabla n_i = 0$ we obtain:⁴

$$\mathbf{E}^{init} = \sum_i \frac{t_i \widehat{\mathcal{S}}_i}{\xi_i e} \nabla T = \mathcal{S}_e^{init} \nabla T, \quad (10)$$

where $t_i = \sigma_i / \sigma_T$ is the Hittorf transport number of ionic species i , *i.e.* the relative contributions of its conductivity σ_i to the total conductivity: $\sigma_T = \sum_i \sigma_i$.

In a thermocell, where a reversible redox reaction occurs at the electrodes, the difference of electrochemical potential between the hot and the cold electrodes at initial state is: $\Delta\tilde{\mu} = -e\Delta V^{init} = e\Lambda^{init}\Delta T$, with⁴ (see Supporting Information III) for more detail):

$$\Lambda^{init} = \frac{\Delta s_r}{e} + \mathcal{S}_e^{init} = \frac{\Delta s_r}{e} + \sum_i \frac{t_i \widehat{\mathcal{S}}_i}{\xi_i e}. \quad (11)$$

The first term $\Delta s_r = s_{Fc^+} - s_{Fc^-}$ represents the redox reaction entropy at electrodes (*i.e.* the differ-

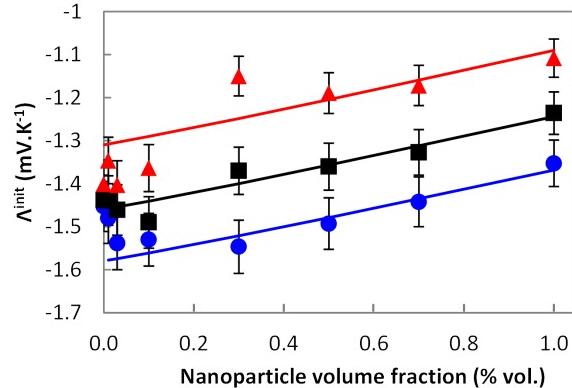


Figure 2: Λ^{init} measured as a function of NP volume fraction ϕ at cell median temperature of 30 (circles), 40 (squares) and 50 °C (triangles). The solid lines are fits to the Eq. (??). See text for more explanation.

ence of the partial molar entropies of F_C^+ and F_C) which remains constant through out the measurements. The second term arises from the initial electric field as described in eq ??.

The measured Λ^{init} , as a function of nanoparticle volume fraction (ϕ), at different temperatures, are shown in Figure 2. The measurements are repeated at least 5 times at each concentration and temperature. The data dispersion is less than 4%. The Λ^{init} values were found negative, as it can be expected from the negative redox reaction entropy of the F_C/F_C^+ couple,²⁹ and varied between -1.1 and -1.6 mV.K⁻¹. The absolute value of Λ^{init} decreases with increasing ϕ as well as with the mean cell temperature.

At a fixed mean cell temperature and constant HClO₄ and F_C/F_C^+ concentrations, the variations in Λ^{init} stems from the term $t\hat{S}(\phi)/(\xi(\phi)e)$ of nanoparticles. The nanoparticles' contribution to the electrical conductivity is: $\sigma = \xi(\phi)Ze^2nD(\phi)/k_BT$ is less than a few percent of the total conductivity σ_T at $\phi \leq 1\%$. The ϕ dependence of σ_T was thus neglected. Combined together, eq ?? can be rewritten as:

$$\Lambda^{init}(\phi) = \Lambda^{init}(0) + \frac{Ze}{k_BT} \frac{\phi}{V_{np}} \frac{D(\phi)}{\sigma_T} \hat{S}(\phi_{eff}). \quad (12)$$

At room temperature, $D(\phi)$ is taken from the linear relation observed through Forced Rayleigh scattering (Figure 1 inset). $\sigma_T = 35.5$ mS.m⁻¹ was measured at room temperature. Since the dominant temperature dependence of both D and σ_T arises from a same quantity *i.e.*: the inverse friction coefficient $1/\eta(T)$ of the solvent, we shall take, as a first approximation, D/σ_T independant of T . The ϕ dependence of $\hat{S}(\phi)$ is obtained from the hard sphere model (eq ??). With $Z = 30$ and $d = 6.7$ nm, the experimental results (Figure 2) are fitted to eq ?? to deduce \hat{S}_0 . The results are compared in Figure 3 to the \hat{S}_0 value determined from the forced Rayleigh scattering experiments at 23°C. In the explored temperature range \hat{S}_0 determined from the Soret and the Seebeck coefficients measurements are ≈ 75 meV.K⁻¹, *i.e.* three orders of magnitude higher than the Eastman entropy of transfer of small usual electrolyte ions (*e.g.*, 0.12 meV.K⁻¹ for sodium ions in water⁴). This observation supports the idea that the Eastman entropy of transfer play a major role in both

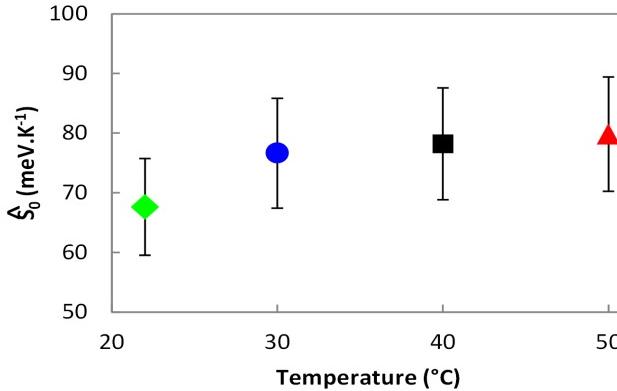


Figure 3: Eastman transport entropy per NP in infinite dilution limit \hat{S}_0 as a function of temperature, estimated by Seebeck (circle, square and triangle) and Soret (diamond) coefficients based models. The large error bars are mainly due to the uncertainty in the average NP size (see text).

thermoelectric and thermodiffusive phenomena in charged colloidal solutions.

4. CONCLUSION

In this work, we have measured the thermoelectric coefficient of an ionically stabilized ferrofluid as a function of nanoparticle volume fraction and compared the results to the corresponding Soret effect measurements. As expected, both coefficients depend on the concentration of charged nanoparticles and the values of Eastman entropy of transfer, \hat{S}_0 , determined from both experiments are found to be in fair quantitative agreement. Our results lend strong support to the existing theoretical models describing charged colloidal solutions' thermoelectric and thermodiffusive properties that both depend on \hat{S}_0 . Following the same rationale, one can postulate that the sign and the magnitude of Seebeck and Soret coefficients must depend on several experimental parameters: *e.g.* the relative importance of the Eastman entropy of transfer between nanoparticles and surrounding ions, the concentration of *all* charged species in the solution, and the surface charge of colloidal particles. These extensive parameters can be tuned experimentally to control the thermoelectric coefficient Λ of charged colloidal suspensions, offering a new perspective in future liquid thermocell research.

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Supporting Information Available

(I) Hard core interactions, (II) Cyclic voltammograms and (III) Initial thermoelectric coefficient. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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- (24) Here the “Eastman entropy of transfer” \widehat{S}_i is understood from Onsager equations.⁴ $\widehat{S}_i = \bar{\bar{S}}_i - s_i$, where s_i represents the partial molar entropy and $\bar{\bar{S}}_i$ is the coefficient of the particle current \mathbf{J}_i in the expression of the entropy current $\mathbf{J}_S = \sum_i \bar{\bar{S}}_i \mathbf{J}_i - \kappa \nabla T / T$; (the last term is the Fourier contribution with heat conductivity κ) .
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